Ceramic Supported Facilitated Transport Membranes for the Separation of Carbon Dioxide and Nitrogen

Uma Maheswari[1], K. Palanivelu[2]

[1]*Centre for Environmental Studies, Anna University, Chennai-600 025, India,*
[2]*Centre for Climate Change and Adaptation Research, Anna University, Chennai-600 025, India,*
2Presenting Author: uma.maheswari992@gmail.com

ABSTRACT

In this study, Selective removal of CO_2 gas from N_2 gas stream was studied by the composite membranes, in which cross linked polyvinyl alcohol (PVA/Acetaldehyde) with triethyelenetetramine (TETA 10 wt %) acts as a active layer and ceramic filter acts as a support layer. The prepared membrane was characterised by Scanning Electron Microscope (SEM). The gas transport properties of the membranes, including gas permeance, flux and selectivity were investigated by using pure CO_2 and N_2 and by varying the parameters such as cross linking agent and membrane thickness. The permeance of both CO_2 and N_2 gas decreases with increase in cross linking agent and membrane thickness, whereas the selectivity was found to be increased. Under optimized conditions the maximum permeability of 69 GPU and selectivity of 50 was obtained. The membrane was found to be stable for 120 hours.

Keywords: Carbon Dioxide, Facilitated transport membranes, TETA, PVA

1. INTRODUCTION

Concern for the changing climate and emission of greenhouse gases, especially CO_2, has resulted in the acceleration of innovative solutions for CO_2 capture and sequestration [1]. IPCC claims [2] that burning of fossil fuel is the primary source of this increased atmospheric concentration of CO_2. According to their report the global surface temperature is likely to increase by 1.1 to 6.4°C between 1990 and 2100. Hence, it is very important from both the environmental and the economical point of views to find an efficient way for separating carbon dioxide from flue gas to minimize its emission into atmosphere. Among various solutions, membranes for CO_2 capture is a low cost, energy saving and environmental friendly process compared to other conventional process [3, 4]. Membranes may be prepared from various types of materials, but currently only polymeric membranes are commercially available for gas separation [5]. Despite, they are stable in nature, the permeability of CO_2 gas through polymeric membranes is less. This could be enhanced by Facilitated Transport Membranes (FTM) [6]. FTMs are the membranes, in which the carrier containing special affinity towards CO_2 gas has been incorporating into the polymeric membrane which gives high permeability and selectivity.PVA is a polyhydroxy and water soluble polymer. It is used for many practical applications due to their ease of its preparation as well as its excellent physical properties and film forming ability, good compatibility with amine, hydrophilic nature. In this study, the facilitated transport of CO_2 through the TETA incorporated polymeric membrane, supported by ceramic filter was studied. The morphology of the composite membrane was observed by Scanning Electron Microscope (SEM). The effect of cross linking agent and membrane thickness on the permselectivity was also examined.

2. EXPERIMENTAL

2.1. Materials

The amine (TETA) was purchased from the Merck Company with 96-98% purity. Poly (vinyl alcohol) (PVA) (99%+ hydrolyzed; Mw = 1, 25,000) was purchased from fisher scientific company, India. The chemicals were used without further purification. Commercially available ceramic water filter is used as a membrane support (height=18.5 cm, radius=2.5 cm). Research grade carbon dioxide (99 % pure) and nitrogen (99 %pure) gases were purchased from Supreme Engineering Services. India.

2.2. Membrane preparation

PVA solution (10 wt.%) was prepared by dissolving pre-weighed dry PVA in water followed by heating at 90^{o}C for six hours with vigorous stirring on a tightly capped glass container [7,8]. Then the solution was allowed to cool down to 70^{o}C. Then a certain amount of acetaldehyde was added into the polymer to obtain PVA cross-linked solution. The PVA/ acetaldehyde solution was heated at about 80ºC for 6 hrs under stirring. Afterwards, TETA (10 %) was added into the polymer solution to achieve desired amine concentration. Thereupon, the amine-PVA blend was stirred continuously followed by heating at 60ºC for 12 hrs. The solution was then cooled to room temperature for at least three hours, and then allowed to stand for at least one day before casting. The ceramic filter was boiled in a hot water and dried at 100^{0}C in an oven for one hour and kept at atmosphere for 24 hours for drying. Then, the PVA-amine blend solution is coated on the ceramic filter. The membrane was further dried at room temperature for at least 24 hours before being used for permeation test.

2.3. Gas permeation measurement

The set-up of the gas permeation experiments using the facilitated transport membranes is shown in Fig.1. The apparatus consisted of a cylindrical-type stainless steel membrane cell with permeation area of 942 cm^2, a gas flow system (canister) that delivered CO_2 and N_2 gas and pressure gauges.

The feed pressure was152 kPa (P_0), while the downstream/permeate was vented to the atmosphere (P_L). The permeate flow rates were measured by volume displacement using a volume flow gas analyzer. All experiments were performed at room temperature (296-298 K). Each experiment was repeated at least twice. Steady-state permeation was determined by permeate flow rate (V/t) measurements made at 30-minute intervals. Steady state was assumed to have reached when the flow rate no longer changed with time.

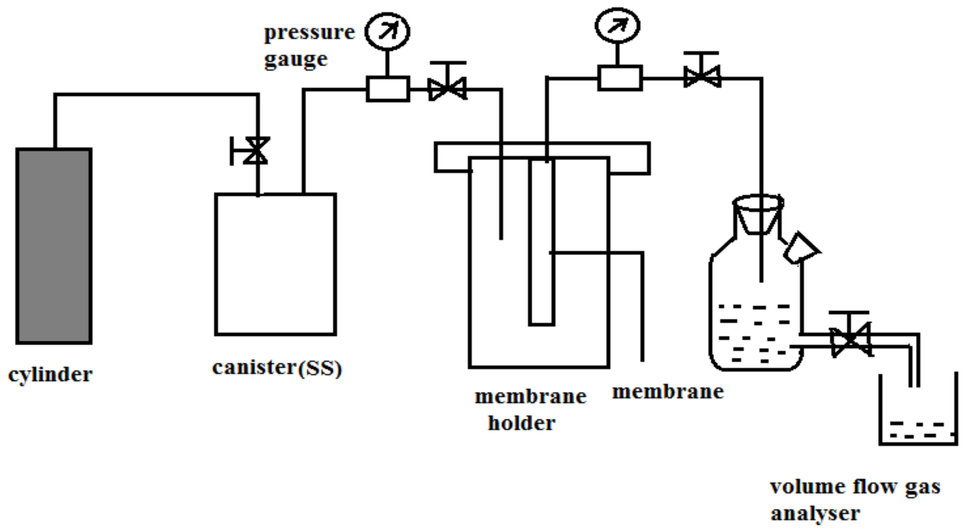

Fig.1. Schematic diagram of the experimental set up

The experimental steady-state permeance through the membrane is calculated as follows [9, 10].

$$J = \frac{273.15}{T}\frac{V}{t}\frac{1}{A}\frac{1}{P_0 - P_L} \longrightarrow (1)$$

The selectivity of carbon dioxide over nitrogen is calculated as the ratio of carbon dioxide permeance to nitrogen permeance.

$$\alpha = \frac{J_{CO_2}}{J_{N_2}} \longrightarrow (2)$$

ISBN: 978-93-83083-87-9

3. RESULTS AND DISCUSSION

3.1. Morphology analysis by SEM:

Figure 2 (a) depicts the surface of ceramic filter before coating. Figure 2(b) illustrates the front surface of PVA-amine blend coated ceramic filter. As can be observed, no macrovoids exist and the homogeneous pattern is created. Furthermore, the ceramic filter pores were totally filled with the PVA-amine blend. Consequently, a nonporous structure was created due to the penetration of PVA-amine blend into the pores of support. Figure 2(c) shows the cross section of the membrane. A thin layer of PVA blended with amine was formed on the top surface of ceramic filter support.

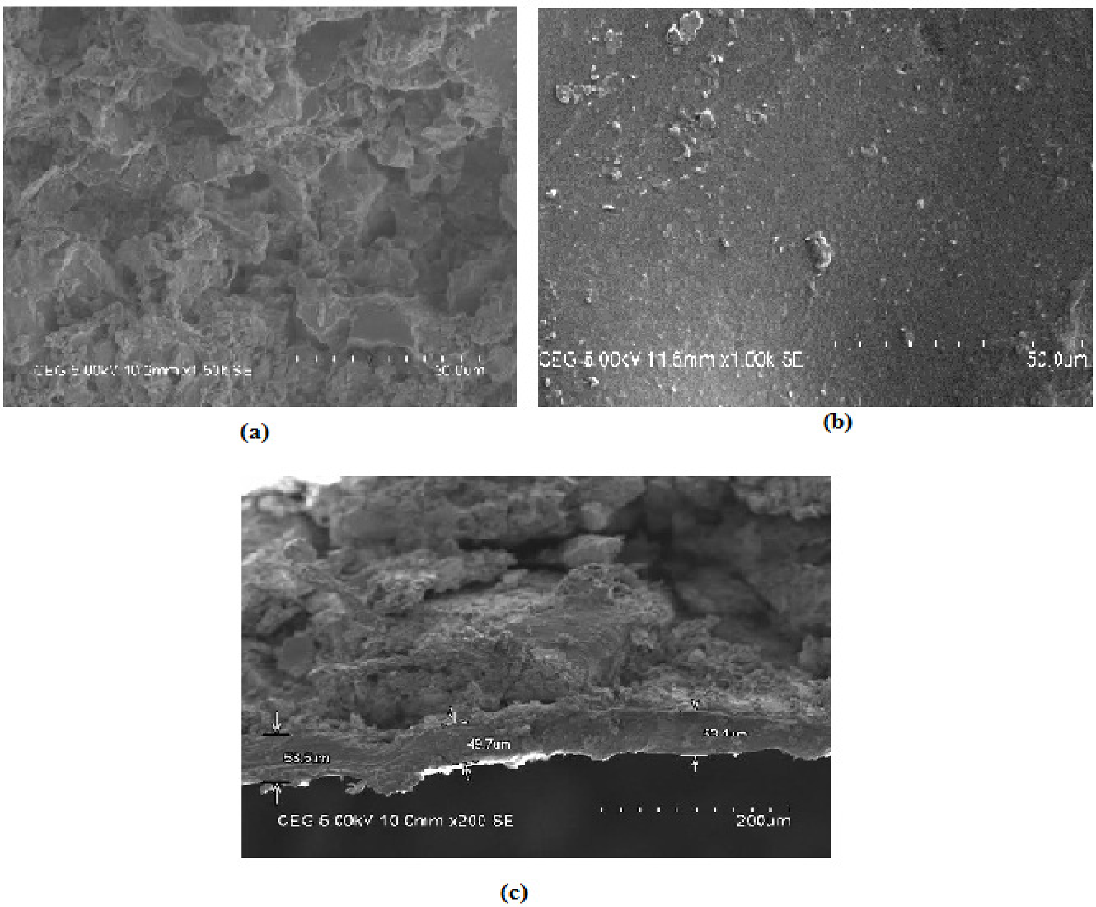

Fig.2.SEM pictures of the top and cross-section of the membranes. (a) Ceramic filter support without coating (b) after coating PVA-TETA (10 wt %) (c) Cross section of PVA-TETA (10 wt %) coated ceramic filter support

3.2. Effect of cross linking agent

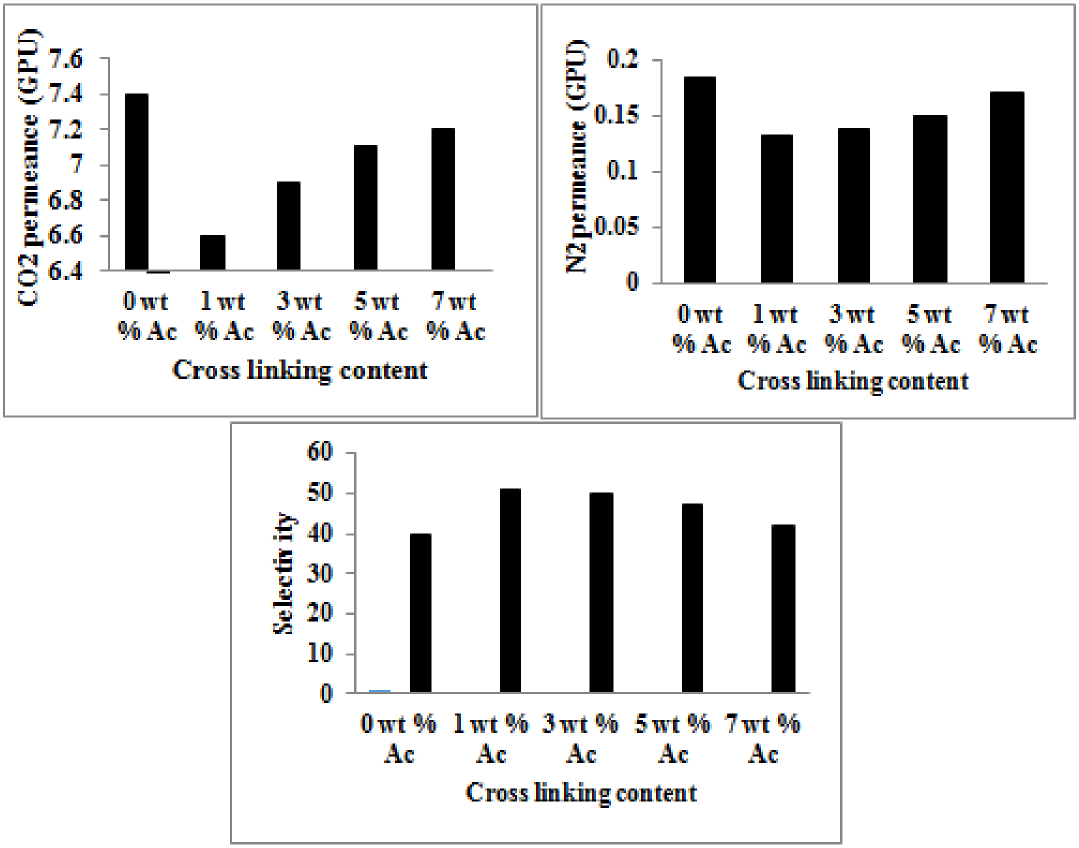

Fig.3. Effect of cross linking agent on the permeability and selectivity of CO_2 gas

The effect of cross linking agent on the permeance of CO_2 and N_2 and selectivity is illustrated in Fig.3. The PVA/Acetaldehyde ratio was varied from 1 wt % to 7 wt %. In general, with increasing PVA/Acetaldehyde mass ratio, CO_2 and N_2 permeances were decreased in comparison with uncross-linked membranes. However, the permeance increased significantly with the increase in cross linking content but the selectivity decreased beyond the cross linking concentration of 3 wt %This trend indicates that low Acetaldehyde content has led to probable higher cross-linking densities. [11, 12]

3.3. Effect of Membrane thickness:

Membrane thickness is likely to have an effect on CO_2 transport across the membrane. To investigate this concept, four membranes were prepared with effective thickness of about 36, 42, 55

ISBN: 978-93-83083-87-9

and 64 µm respectively and it is presented in Fig. 4. Variations in thickness were achieved by repeatedly casting the polymer solution into the substrate. Both CO_2 and N_2 permeance decreases with an increase in the membrane thickness because the diffusion rate in the membrane is inversely proportional to the membrane thickness [13, 14]. The membrane thickness is likely to have an impact on the selectivity between CO_2 and N_2. For thicker membranes (i.e. 55 and 62 µm), the residence time of CO_2 was longer so that it consumes more TETA to react with. The effect was greater facilitation leading to an increase in selectivity.

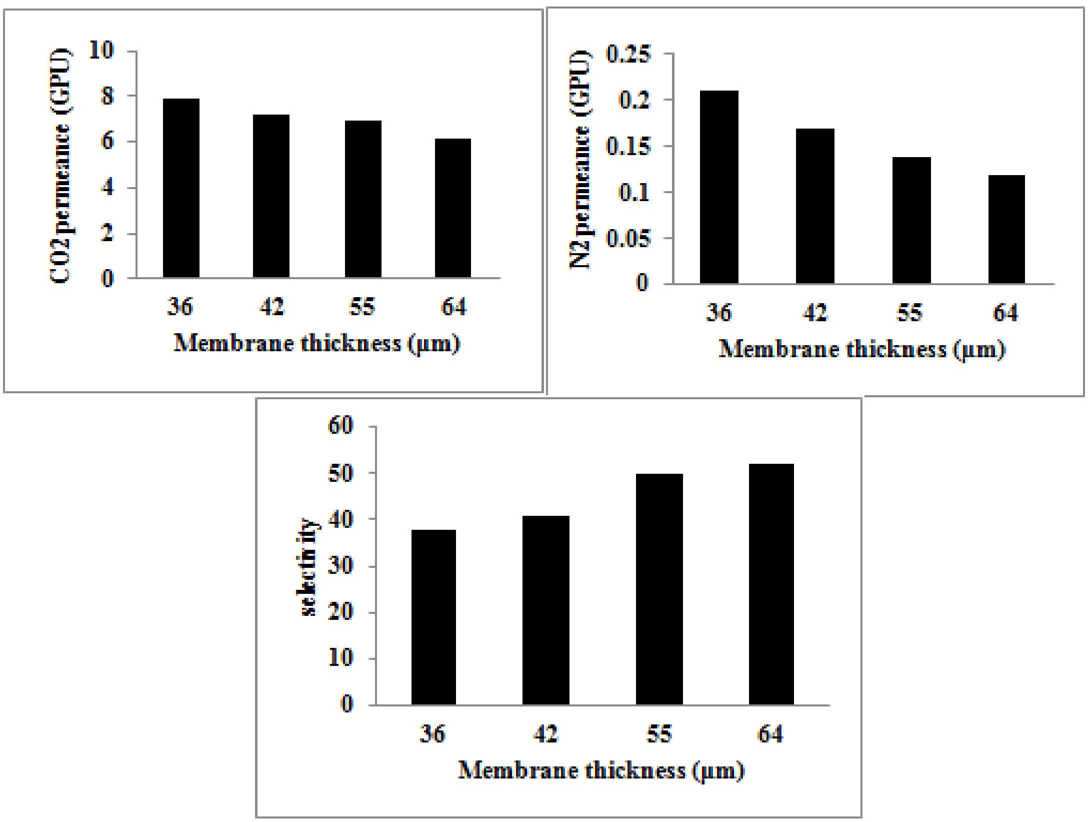

Fig. 4. Effect of Membrane thickness on the permeability and selectivity of CO_2 gas

3.4. Stability of Membrane:

In evaluating the practicality of these facilitated transport membranes for CO_2 separation, one parameter of paramount importance is the membrane lifetime. As shown in Fig 5. the membrane showed roughly constant permeance up to 120 hours. Beyond that the permeance decreased due to

ISBN: 978-93-83083-87-9

the membrane drying. This decrease in membrane performance could be regenerated by introducing certain amount of water into the permeation unit.

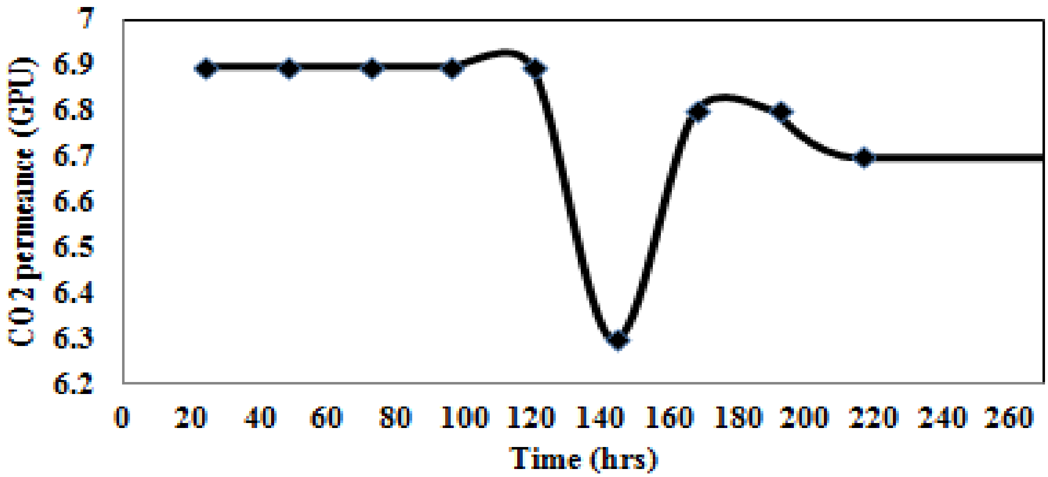

Fig. 5. Permeance of CO_2 as a function of time

4. CONCLUSION

Selective removal of CO_2 gas from N_2 of both CO_2 and N_2 gas decreases with increase in cross linking agent and membrane thickness, whereas the gas stream was studied by the composite membranes, in which cross linked polyvinyl alcohol (PVA/Acetaldehyde) with triethyelenetetramine (TETA 10 wt %) acts as a active layer and ceramic filter acts as a support layer. The parameters such as cross linking agent content and the membrane thickness have been optimized. The PVA/Acetaldehyde ratio of 3 wt % and the membrane thickness of 55 µm were found to give the maximum permeability. Under optimized conditions the maximum permeability of 69 GPU and selectivity of 50 was obtained. The membrane was found to be stable for 120 hours.

5. ACKNOWLEDGEMENT

One of the authors (AUM) would like to acknowledge the financial support provided by the **DST-INSPIRE (IF 10580),** New Delhi, India for this research work.

REFERENCES

[1] C.E. Powell, G.G. Qiao. Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. J.Membr.Sci. 2006; 279:1–49.

[2] IPCC 2011, Summary for Policymakers, in IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation, O. Edenhofer, Pichs- Madruga R., Sokona, Y., Seyboth, K., Matschoss,

P., Kadner, S., Zwickel, T., Eickemeier, P., Hansen, G., Schlömer, S., von Stechow, C., Editor, Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

[3] T. Yamaguchi, L.M. Boetje, C.A. Koval, R.D. Noble, C.N. Brown. Transport properties of carbon dioxide through amine functionalized carrier membranes. Ind. Eng. Chem. Res. 1995; 34:4071–4077.

[4] H. Matsuyama, M. Teramoto, H. Sakakura. Selective permeation of CO_2 through poly {2-(N,N-dimethyl) aminoethyl methacrylate} membrane pre- pared by plasma-graft polymerization technique. J.Membr. Sci. 1996; 114:193–200.

[5] R. Quinn, D.V. Laciak, G.P. Pez. Polyelectrolyte-salt blend membranes for acid gas separations. J. Membr. Sci. 1997; 131: 61–69.

[6] H. Matsuyama, A. Terada, T. Nakagawara, Y. Kitamura, M. Teramoto. Facilitated transport of CO_2 through polyethylenimine/poly (vinyl alcohol) blend membrane. J. Membr. Sci. 1999; 163:221–227.

[7] J.H. Meldon, P. Stroeve, C. Gregoire. Facilitated transport of carbon dioxide: a review. Chem. Eng. Commun. 1982;16:263–300.

[8] A. Aroonwilas, A. Veawab. Characterization and comparison of the CO_2 absorption performance into single and blended alkanolamines in packed column. Ind. Eng. Chem. Res., 2004; 43:2228–2237.

[9] M. Teramoto, Q. Huang, T. Watari, Y. Tokunaga, R. Nakatani, T. Maeda, H. Matsuyama. Facilitated transport of CO_2 through supported liquid membranes of various amine solutions-effects of rate and equilibrium of reaction between CO_2 and amine. J. Chem. Eng. Jpn. 1997; 30:328– 335.

[10] T. Yamaguchi, C.A. Koval, R.D. Noble, C.N. Bowman. Transport mechanism of carbon dioxide through perfluorosulfonate ionomer membranes containing an amine carrier. Chem. Eng. Sci. 1996; 51: 4781– 4789.

[11] Z. Wang, C. Yi, Y. Zhang, J. Wang, S. Wang. CO_2-facilitated transport through poly(N-vinyl-sodium amino butyrate-co-sodium acrylate)/polysulfone composite membranes. J. Appl. Polym. Sci. 2006; 100:275–282.

[12] B.C. Tripp, K. Smith, J.G. Ferry. Carbonic anhydrase: new insights for an ancient enzyme. J. Biol. Chem. 2001;276:615–618.

[13] A.L. Crumblis, K.L. McLachlan, J.P. O'Daly, R.W. Henkens. Preparation and activity of carbonic anhydrase immobilized on porous silica beads and graphite rods. Biotech. Bioeng. 1988; 31:796–801.

[14] L.H. Bao, M.C. Trachtenberg. Modeling CO_2 facilitated transport across a diethanolamine liquid membrane. Chem. Eng. Sci. 2005; 60:6868–6875.